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(54) Title: PROCESS TO MAKE LOW-MOLECULAR WEIGHT SMA (57) Abstract The invention pertains to a process to make low-molecular weight (block) copolymers of one or more vinyl and one or more maleic monomers, by radically polymerizing said monomers in the presence of an initer.		

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PROCESS TO MAKE LOW-MOLECULAR WEIGHT SMA

- 5 The present invention relates to a process to make (block) copolymers of vinyl and maleic monomers with a low molecular weight.

Low-molecular weight copolymers of vinyl and maleic monomers, typically comprising styrene and maleic anhydride (LW-SMA), are used in a variety of applications for various purposes. It is known that they can act as pigment
10 dispersant, viscosity modifier, compatibilizer, emulsifier, protective colloid, and the like. Whether they can be used and if so, how efficiently, depends to a large extent on the molecular weight and the molecular weight distribution of the copolymer.

- 15 For this reason there have been significant efforts to develop processes that allow control over the molecular weight when copolymerizing styrene and maleic anhydride. BE 710138, published in 1968, discloses a process for producing LW-SMA by cotelomerizing the monomers at 150-270°C, using specific telogens (solvents that act as chain transfer agents), without the
20 addition of radical-forming activators and solely under the influence of heat. US 3,451,979 (1969) discloses a polymerization process at 175-250°C wherein the molecular weight is controlled by using monocyclic hydrocarbons having a nucleus of 6 carbon atoms, such as cumene and p-cymene, as a solvent. In DE-OS-1 930 217, published in 1970, it is proposed to make LW-SMA by
25 using specific hydroxyalkyl mercaptans in a solution or precipitation polymerization process. US 4,180,637 (1979) discloses a solvent polymerization process wherein LW-SMA is produced by using a hydroxide or a nucleophilic salt of a monovalent ammonium or alkali metal cation. Finally, DD-A 259 408 (1988) discloses a solvent polymerization process at 40-100°C

wherein LW-SMA is produced by using a chain transfer agent which is a derivative of a thiocarbonic acid.

It is observed that in all of these processes of the prior art, either a reactive
5 solvent (a solvent with chain transfer activity) or specific chain transfer agents (CTAs) are proposed. However, to our knowledge, reactive solvents typically are not used, since they will contaminate the resulting polymer or will require extensive drying steps for their removal from said polymer. Also, the use of sulfur- or metal-containing CTAs is limited to applications wherein the
10 presence of such atoms can be tolerated. In this respect we would like to mention that LW-SMA comprising a sulfur-containing CTA may suffer from discolouration, unpleasant smell, and/or accelerated ageing.

Besides these disadvantages, we have found that none of these processes allows for an accurate prediction of the molecular weight of the resulting
15 polymer. Typically, a trial and error approach is needed to find the necessary concentration of reactants under certain reaction conditions. Needless to say, changing one of the parameters of the process (e.g. temperature, in an effort to optimize reactor output) will make it necessary to again optimize the process to obtain LW-SMA with the desired molecular weight. Such continuous
20 optimization not only requires time and effort but also results in waste product not meeting the specifications.

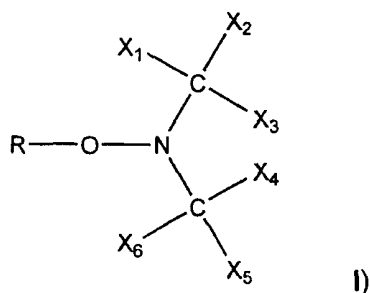
Also, the LW-SMA of the prior art is not easily modified further when a certain use demands different properties. Particularly in the field of compatibilization, the various uses often require a compound with properties that are only
25 partially met by the known LW-SMAs. Hence there is a need for LW-SMAs that can easily be modified.

Furthermore, it is well-known that in conventional LW-SMA production processes, the styrene and the maleic anhydride monomer will have a strong preference for copolymerization in an alternating form. This means that if the
30 monomer feed deviates from a molar ratio of 1:1, depending on the process

conditions, first an alternating copolymer and later a homopolymer is formed of the excess monomer (resulting in two distinct polymers that are difficult to separate and of which only one type has the desired properties). If the surplus monomer does not homopolymerize, this monomer's conversion rates will be correspondingly low and it will contaminate the formed copolymer. Both results are undesired.

Surprisingly, we have now found a new polymerization process wherein the disadvantages are largely overcome. It was found that just one type of copolymer is formed, irrespective of the monomer ratio, and that the molecular weight of the LW-SMA is very close to easily calculated theoretical values, resulting in substantially reduced optimization efforts and that block copolymers with desired properties can be obtained.

The process is characterized in that use is made of a specific type of molecular weight control agent, viz. initiators. Preferably, the initiators used have a structure according to formula I):



wherein:

- ♦ R represents a group which has at least one carbon atom and is such that the free radical $R\cdot$ is capable of initiating the free radical polymerization of unsaturated monomers;
- ♦ at most five of the groups represented by X_1 - X_6 are the same or different linear or branched, substituted or unsubstituted (cyclo) alkyl groups, and/or

two or more of the groups X_1 - X_6 may be linked to form cyclic structures comprising the -CNC- moiety,

- ♦ the complementary groups X_1 through X_6 are functional groups independently selected from substituted or unsubstituted aryl, cyano, nitro, dialkoxyphosphonyl, $R'O-$, $R'OC(O)-$, $R'C(O)O-$, $R'C(O)OC(O)-$, $R'R'NC(O)-$, $R'C(O)NR'-$, $R'C(O)NR'C(O)-$, and $R'C(O)-$, wherein each of R' is, independently, hydrogen or a substituted or unsubstituted hydrocarbyl group, or, alternatively, $-CX_1X_2X_3$ and/or $-CX_4X_5X_6$ represent a substituted or unsubstituted aryl group.
- 10 However, also conventional initiators may be used, such as products with a tetramethylpiperidinoxy (TEMPO) moiety. Furthermore, as is known in the art, it is possible to combine a peroxide and a conventional stable free radical agent to form an initiator *in situ*. In such cases the preferred ratio of peroxide to stable free radical agent is about 1:2 on a molar basis, so that each of the two
- 15 radicals formed during decomposition of the peroxide can be linked to one stable free radical.

The hydrocarbyl groups R' of the preferred initiators may independently be either alkyl, aryl, alkaryl, aralkyl, and/or cycloalkyl. Preferably, the substituted or

20 unsubstituted hydrocarbyl group contains less than 30, more preferably less than 15, atoms.

The term "initiator" as used herein defines compounds that can initiate and control a polymerization reaction by thermal decomposition, optionally in the

25 presence of an accelerator. The initiator must be capable of forming, upon thermal decomposition, two radical fragments of which one must have the predominant tendency to initiate the polymerization reaction, i.e. by forming a stable covalent bond with a monomer molecule thereby transferring the radical to said monomer, whereas the other radical fragment is predominantly a stable

30 free radical as is known in the art. Preferred compounds are of formula I). It is

believed that the carbon-centred radical formed upon decomposition initiates the polymerization, whereas the nitroxide radical will function as a stable free radical, terminating the growing chain. Without the invention being limited to such a theory, it is further believed that the termination reaction is reversible at
5 the polymerization temperature, so that monomers can be inserted between the last monomeric unit and the nitroxide moiety of the initer. This sets these types of compounds apart from regular chain transfer agents which terminate a growing chain and, subsequently, initiate a new, separate chain.

10 It is noted that the preferred initiators are described in International application No. PCT/EP97/05009 of the same applicant. However, it is not disclosed therein that these compounds are particularly suitable for the production of LW-SMA (block) copolymers and that by using the compounds for this particular class of polymers, all the disadvantages of the prior art can be
15 overcome.

Presumably, the polymerization process according to the invention is a "pseudo-living polymerization process," which term stands for the radical polymerization process in which ethylenically unsaturated monomers are
20 polymerized by means of at least one initer. According to a non-limiting theory, the polymerization kinetics in such a process depend, amongst others, on the thermal decomposition rate of the initer that is used.

With respect to the initiators of formula I), it is preferred that X_1-X_6 are not linked
25 to form cyclic structures. Furthermore, it is preferred that each of X_1-X_6 contains fewer than 30 carbon atoms. More preferably, each of X_1-X_6 contains fewer than 10 carbon atoms, in order to produce initiators with a low molecular weight. Most preferably, at most five of X_1-X_6 are independently selected from methyl, ethyl, propyl, isopropyl, butyl, sec.butyl, tert.butyl, and cyclohexyl.

- Furthermore, it is preferred that the process involves the use of initiators of formula I) wherein the functional group is selected from substituted or unsubstituted aryl, cyano, dialkoxyphosphonyl, $R'C(O)O-$, and $R'OC(O)-$. Of the aryl groups, phenyl, tolyl, and naphthyl are preferred. More preferred is a process wherein the initiator possesses a cyano, phenyl, $R'C(O)O-$ or dialkoxyphosphonyl group. Even more preferred is a process where the initiator possesses a cyano or phenyl group. Preferably, these initiators can be used without toxic by-products being formed.
- 10 Non-limiting examples of functional groups of the initiator further include methylether, ethylether, propylether, butylether, poly(alkylether), methylketone, ethylketone, propylketone, isopropylketone, butylketone, isobutylketone, tert.butylketone, diethoxyphosphonyl, ethoxypropoxyphosphonyl, dipropoxyphosphonyl, dibutoxyphosphonyl, diisobutoxyphosphonyl, $-C(O)OCH_3$,
15 $-C(O)OC_2H_5$, and C_1-C_{20} carboxylic acid esters.

- The R group may bear one or more of the $ONC(X_{1-3})C(X_{4-6})$ functions, as long as each of the radicals $R\cdot$ formed upon the scission of one or more of the R-O bonds is capable of initiating the free radical polymerization of an unsaturated monomer. Furthermore, it is preferred that R is not of a polymeric nature, meaning that R preferably does not comprise more than approximately 4 recurring units incorporated through radical polymerization of one or more unsaturated monomers. Preferably, R does not contain more than two of such recurring units. Most preferred are compounds wherein R equals $C(X_{1-3})$ or
20 $C(X_{4-6})$.
25

- The process to make the LW-SMA can be conducted at various temperatures, typically ranging from 50 to 200°C. More preferably, the polymerization temperature is from 80 to 150°C. Depending on the polymerization
30 temperature that is chosen, an initiator or, less preferably, a combination of a

conventional stable free radical agent and a peroxide, with an acceptable decomposition rate is selected. From, for instance, *Macromolecules*, **1995**, 28, 8722-8728, it is known that the use of electron-withdrawing functional groups will stabilize the R-O bond of the preferred initiators, whereas electron-donating functional groups will labilize it. Given this information and the teaching of this document, the man skilled in the art will have no problem selecting suitable types and numbers of functional groups to obtain usable initiators. Before conducting actual polymerization experiments, the half-life of the preferred initiators may be determined in one or more well-known ways, this in order to establish at which temperature it can be used.

The amount of initiator to be used in the process according to the invention depends on the molecular weight of the resulting LW-SMA that is desired. More specifically, the process according to the invention results in polymers with a number average molecular weight (M_n) close to the theoretical value (M_{th}), calculated from $(M_{initiator} + [monomer]/[initiator] * M_{monomer}) * conversion$, wherein $M_{monomer}$ is the average molecular weight of the repeating monomeric units. For a perfectly alternating styrene maleic anhydride copolymer $M_{monomer}$ is about $(104+98)/2 = 101$. Because LW-SMAs are generally considered to be polymers having a molecular weight from about 1000 to about 20 000 Dalton, this means that ideally the molar amount of initiator to be used is about 0.1 to 0.005 times the molar amount of monomer. In practice, the molar amount of initiator will vary from 0.15 to 0.001 times the molar amount of monomer in the polymerizing system. More preferably, the molar amount of initiator is from 0.12 to 0.005 times the molar amount of monomer.

The ethylenically unsaturated monomers typically polymerized in the process according to the invention are styrene and maleic anhydride. However, the process according to the invention is not limited to a process wherein only these two monomers are employed. Instead of maleic anhydride also other

- maleic monomers like citraconic anhydride, itaconic anhydride, maleic acid, fumaric acid, citraconic acid, itaconic acid, half-esters of said acids with C₁-C₁₈ monohydric alcohols, such as methyl maleate and sec.butyl maleate, maleimides, citraconimides, itaconimides, and/or mixtures of these monomers, optionally together with maleic anhydride, can be used. Similarly, (part of) the styrene may be replaced by other vinyl monomers like α -olefins; isoprene; butadiene; acrylonitrile; vinyl chloride; vinyl esters of organic acids, such as vinyl acetate and vinyl stearate; (alkyl)(meth)acrylic acid or esters thereof, such as methylmethacrylate; vinyl phosphonic acid or esters thereof; vinyl pyridine; vinyl alkyl ethers, such as vinyl methyl ether and vinyl isobutyl ether; and other vinyl aromatic compounds or derivatives thereof, such as styrene phosphonic acid, styrene phosphonic esters, vinyl toluene, vinyl xylene, 2,4-dimethylstyrene, 2,5-dichlorostyrene, 2-methyl-4-chlorostyrene, and so forth. Preferably, at least styrene and maleic anhydride are used in the process according to the invention. More preferably, the amount of both maleic anhydride and styrene is at least 10% by weight of the final polymer. Most preferred is a process resulting in an LW-SMA containing at least 30% w/w of styrene and maleic anhydride.
- The molar ratio between the two types of monomers in the process is not critical. Independent of the ratio that is used, essentially one type of polymer is formed. If one monomer is used in excess, this monomer, depending on its structure, will homopolymerize at a later stage in the process to form a separate block which is attached to the polymer formed in the previous step when both types of monomers were still present. This is in contrast to, for instance, conventional batch polymerization processes, where the excess monomer is formed as a homopolymer which is not attached to previously formed copolymer. Therefore, when the molecular ratio of the first formed polymer does not equal the monomer ratio of the monomer feed, the process of the invention will result in a block copolymer with blocks having an

alternating styrene-maleic anhydride structure and a block with a different structure, depending on the monomer type and ratio used. In order to obtain an LW-SMA with the desired properties, it is preferred that the ratio of vinyl to maleic monomer ranges from 0.6 to 5, with a ratio between 0.8 and 3 being
5 more preferred. Because styrene blocks, attached to the alternating styrene-maleic anhydride copolymer, are easily formed, it is preferred to use a slight molar excess of styrene vis-à-vis maleic anhydride.

If so desired, it is possible to introduce new monomer(s) into the polymerizing
10 system, preferably after more than 50, more preferably more than 90% w/w, of the LW-SMA monomers have reacted, in order to create a block copolymer having an LW-SMA block and a block consisting of one or more of the monomers present after the introduction of the new monomers. What type of block will be formed will depend to a large extent on the copolymerization
15 parameters of the monomers that are present. Such a step may be repeated to create block copolymers having three or more distinct types of blocks in the molecule. Preferably, the newly added monomers are selected from the vinyl monomers as described above. The building of such block copolymers is not possible with the LW-SMAs of the prior art, since the polymerization in
20 conventional processes is terminated by chain transfer, disproportionation or combination reactions. It is believed that in the process according to the invention, the nitroxide moiety of the initer, as indicated above, remains at one end of the polymer chain and allows the further insertion of monomer when such monomer is introduced. Preferably, the LW-SMA blocks have a
25 combined length of at least 5, preferably more than 10, monomeric units (of either type of monomer) before the next block is formed.

Although the process according to the invention can be conducted in various ways, e.g. as mass, suspension, emulsion, or solvent polymerization, a solvent
30 polymerization process is preferred. More preferably, the process is a solvent

polymerization process wherein the solvent is non-reactive, meaning that less than 5% of all end groups of the resulting polymer consists of a solvent moiety. The total concentration of monomer in said solvent polymerization process can vary over a wide range and is only limited by reactor efficiency and the solubility of the monomer (and formed polymer) in the solvent. More specifically, the solubility of the monomer/polymer will depend on the type of solvent, the temperature, and the monomer type and ratio used. Typically, concentrations of monomer of less than 10% by volume (% v/v) are considered to be uneconomical, whereas concentrations of over 85 % v/v typically result in viscosity / solubility problems. A preferred monomer concentration therefore is 20-65% v/v, based on the total volume of solvent and monomer.

Solvents that can be used in the process according to the invention include, but are not limited to, ethers, such as dioxane and tetrahydrofuran; ketones, such as acetone, methylethyl ketone, and the like; esters, such as ethyl acetate and methoxypropyl acetate; aromatic solvents, such as toluene and xylene; products like dimethyl formamide and nitropropane; as well as mixtures thereof.

20

In the preferred process according to the invention, wherein initiators are used, use may be made of further additives such as conventional radical generating species, including organic peroxides, azo-initiators and UV-initiators; stable free radicals; and chain transfer agents. Also, use can be made of accelerators, additives catalyzing the decomposition of radical forming species as used in the process. Furthermore, if so desired, adjuvants like pigments, stabilizers, colloids, fillers etc. may be added at the start or during the polymerization, as long as they do not interfere in the polymerization process. Alternatively, the adjuvants are added to the polymer (solution) after the polymerization.

30

- The initiators as used in the process according to the invention may be produced in various conventional ways as described in, for instance, *J. Chem. Soc.*, **1954**, 1920-1924). Reactants and reaction conditions are chosen such that
- 5 during the synthesis at least one of the two carbon-centred radicals attached to the nitrogen atom will bear a functional group. This is most easily achieved by selecting the proper concentration of one or more of the functional group bearing carbon-centred radical precursors. Preferably, the functional group bearing carbon-free radical is obtained by the decomposition of one or more
- 10 appropriate azo, C-C or other initiators such as diacyl peroxides with a high decarboxylation rate. Depending on the use of the initiator, it may be preferable to react only one type of carbon-centred radical (containing a functional group) with the NO gas.
- 15 Alternatively, compounds according to the invention can be produced by the well-known reaction of a nitroso compound under influence of heat or with carbon-centred radicals, as described by T. Kolasa, A. Chimiak, and A. Kitowski in *J. Prakt. Chem.*, **1975**, 317, 252-256.
- 20 The invention will be further illustrated by the following examples.

Experimental

- The chemicals used in the following examples were all reagent grade unless
- 25 specified otherwise. Styrene was supplied by Baker (Baker PA grade). The styrene was freed of inhibitor by a treatment with an alkaline Al_2O_3 column before use. Methyl isobutyl ketone (MIBK) solvent was supplied by Fluka. Perkadox® AIBN (2,2'-azobis[isobutyronitrile]), Lucidol® (75% dibenzoyl peroxide, 25% water), as well as the initiators that were used, were supplied by
- 30 Akzo Nobel or synthesized as laid down in the available documentation.

The conversion of monomer into polymer was determined in conventional ways by gas chromatographic (GC) analysis for monomer, using monochlorobenzene as the internal standard.

5

The number average molecular weight (M_n), the weight average molecular weight (M_w), and the dispersity (D) of the polymers were analyzed in conventional ways by means of size exclusion chromatography, using THF as the eluent. Polystyrene samples were used as calibration standards.

10

Polymers were isolated from the solution by precipitation in *n*-pentane and subsequent drying to constant weight in a vacuum oven at 50°C (20-100 hours).

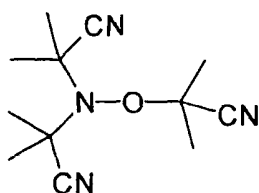
15 Polymers were occasionally further characterized by means of 300 or 400MHz ^1H and 100 MHz ^{13}C NMR.

No attempt was made to optimize yields.

20 Example 1

Preparation of initiator

N,N,O-Tris-(1-cyano-1-methylethyl)hydroxylamine ((IBN) $_3$ NO)



25

A solution of Perkadox AIBN (152.7 g, 0.93 mol) in 1500 ml of toluene was stirred, flushed with nitrogen gas, and heated to 76°C. A stream of nitrogen

monoxide (5 l/hr) was passed through the solution, and a deep greenish/blue colour appeared. Heating was continued for 2 hours at 76°C, 1 hour at 82°C, 30 minutes at 88°C, 15 minutes at 94°C, and finally 15 minutes at 119°C to achieve complete decomposition of the AIBN. Residual nitrogen monoxide
5 was removed by flushing the reaction mixture with nitrogen gas, at which point the colouration changed to yellow. The solvent was removed at the rotary evaporator, and the resulting solution was steam-distilled to remove the by-product tetramethyl succinonitrile. Next, the water/product mixture was left to cool down to room temperature, and the product precipitated. This solid was
10 removed by filtration, dissolved in dichloromethane, and then dried with magnesium sulfate. Evaporation of the solvent gave 84.3 g (58%) of a yellow solid, the $(\text{IBN})_3\text{NO}$.

Examples 2-4

Polymerizations were conducted in a 250 ml three-necked flask which was fitted with an argon gas inlet, a reflux condenser, an inlet through which reactants could be added, and a magnetic stirrer. Argon was flushed through
 5 and over the reaction mixture throughout the polymerization. Unless stated otherwise, 60 ml of methyl isobutyl ketone solvent (MIBK) was purged with argon and heated to a polymerization temperature of 114°C. When this temperature was reached, a solution of 9.5 g of styrene, 9.0 g of maleic anhydride, and the various amounts of initer of Example 1, in 20 ml MIBK, was
 10 added in 2 hours at a rate of approximately 0.33 ml/min. Thereafter, the mixture was kept at the polymerization temperature for another 4 hours. The following results were obtained.

Experiment	mol% of initer on monomers	M _{th} (Dalton)	M _n (Dalton)	Styrene conversion (%)
2	4	2760	3200	>99
3	6.7	1740	2000	>99
4	6.7	1740	2200	98

For Example 3, the following results were obtained during the polymerization.

Time (hours)	Styrene conversion (%)	M _n (Dalton)
2	34	1750
3	87	1950
4	96	2050
5	99	2075
6	>99	2050

15

The obtained polymers were odourless.

Examples 5 and 6

Following the same procedure as described for Examples 2-4, a solution of 12.4 g of styrene, 5.8 g of maleic anhydride, and the indicated amount of initer, in 20 ml MIBK, was dosed. The following result were obtained.

5

Experiment	mol% of initer on monomers	M _{th} (Dalton)	M _n (Dalton)	Styrene conversion (%)
5	3.2	2784	3000	80
6	3.2	2944	3200	85

Formation of homopolystyrene was not observed, and the polymer was odourless.

10 Example 7

Using the equipment as described for Examples 2-4, a mixture of 40 ml of MIBK, 25.8 g of maleic anhydride, 27.1 g of styrene, and 2.54 g of initer of Example 1 was purged with argon, heated to 114°C, and reacted at this temperature for 6 hours, with the following result.

15

Experiment	mol% of initer on monomers	M _{th} (Dalton)	M _n (Dalton)	Styrene conversion (%)
7	2	5284	6000	>99

The obtained polymer was odourless.

Example 8

Example 5 was repeated. However, at the end of the 4-hour polymerization, the temperature was maintained at 114°C and 53.4 g of butyl acrylate were dosed to the reaction mixture in two hours. The butyl acrylate had been
5 purified before use in the same way the styrene monomer was purified. After addition of the butyl acrylate, the mixture was further reacted for 4 hours at 114°C.

It was found that 50% of the butyl acrylate was polymerized, while analysis
10 with size exclusion chromatography, using a refractive index and a UV detector, showed that only a single polymer was formed. NMR analysis showed it to comprise both polybutyl acrylate units and styrene maleic anhydride units.

This block copolymer is considered very suitable to serve as a coupling agent.
15

Comparative Examples A and B

Example 5 was repeated, but instead of 6.7% initiator, 3.4% of either dibenzoyl peroxide or AIBN was used. However, in both cases an insoluble polymer with a number averaged molecular weight much higher than 10 000 was rapidly
20 formed.

Comparative Example C

Example 2 was repeated, except that 0.5 mol% of AIBN was used in combination with 5 mol% of dodecyl mercaptan (dodecane thiol), based on the
25 total amount of monomers.

Because the chain transfer activity parameter of dodecyl mercaptan in this polymerization system is not known, it is impossible to predict, without further experimentation, what the molecular weight of the resulting polymer would be. Using the indicated large amounts of both chain transfer agent and azo-
30 initiator was expected to result in a very low-molecular weight SMA. However,

when more than 99% w/w of the styrene was polymerized, the resulting polymer had a number averaged molecular weight of 3500, which was far higher than expected. Furthermore, the obtained polymer had an undesired unpleasant smell.

5

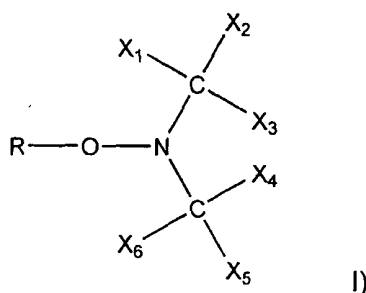
Example 9

Using a three-necked flask of 100 ml, a mixture of 5.17 g (0.022 mole) of (IBN)₃NO, 11.51 g (0.11 mole) of styrene, 10.83 g (0.11 mole) of maleic anhydride, and 25 g of methoxypropyl acetate was flushed with Argon and
10 heated to 120°C by submerging the flask in an oil bath. The flask was kept in the bath for 4 hours at this temperature of 120°C.

The resulting polymer was analyzed by means of GPC with the following results: Mn=1166, Mw=2350, and Mp=2172 Dalton.

Claims

1. A process for preparing low-molecular weight copolymers of one or more vinyl and one or more maleic monomers, by radically polymerizing said monomers in the presence of a molecular weight control agent, characterized in that the molecular weight control agent is an initer.
2. A process according to claim 1 wherein the initer is a compound of formula I)



wherein:

- ♦ R represents a group which has at least one carbon atom and is such that the free radical $R\cdot$ is capable of initiating the free radical polymerization of unsaturated monomers;
- ♦ at most five of the groups represented by X_1 - X_6 are the same or different linear or branched, substituted or unsubstituted (cyclo) alkyl groups, and/or two or more of the groups X_1 - X_6 may be linked to form cyclic structures comprising the -CNC- moiety,
- ♦ the complementary groups X_1 through X_6 are functional groups independently selected from substituted or unsubstituted aryl, cyano, nitro, dialkoxyphosphonyl, $R'O-$, $R'OC(O)-$, $R'C(O)O-$, $R'C(O)OC(O)-$, $R'R'NC(O)-$, $R'C(O)NR'-$, $R'C(O)NR'C(O)-$, and $R'C(O)-$, wherein each of R' is, independently, hydrogen or a substituted or unsubstituted hydrocarbyl group, or, alternatively, $-CX_1X_2X_3$ and/or $-CX_4X_5X_6$ represent a substituted or unsubstituted aryl group.

3. A process according to claim 1 or 2, characterized in that the monomers to be polymerized comprise at least styrene and maleic anhydride.
- 5 4. A process according to claim 3, characterized in that styrene and maleic anhydride are both present in an amount of at least 10% by weight, preferably 30% by weight, of the total monomer composition.
- 10 5. A process according to any one of the preceding claims, characterized in that the initer of formula I) comprises a functional group selected from the group consisting of phenyl, cyano, dialkoxyposphonyl, $R'C(O)O-$, and $R'OC(O)-$, wherein R' has the meaning as defined above.
- 15 6. A process according to claim 5 wherein the functional group is a cyano, phenyl, $R'C(O)O-$ or dialkoxyposphonyl group, more preferably a cyano or phenyl group.
- 20 7. A process according to any one of the preceding claims wherein the polymerization is conducted at a temperature of between 50 and 200°C.
- 25 8. A process according to any one of the preceding claims wherein the molar amount of the initer is from 0.15 to 0.001 times the molar amount of monomer.
9. A process according to any one of the preceding claims wherein the molar ratio of vinyl monomer to maleic monomer ranges from 0.6 to 5.0.

10. A process according to any one of the preceding claims, characterized in that the polymerization is conducted in a solvent which dissolves both monomers.
- 5 11. A process according to any one of the preceding claims wherein one or more ethylenically unsaturated monomers are added after a copolymer of vinyl and maleic monomer has been formed, to produce a block copolymer comprising at least one such LW-SMA block.
- 10 12. A process according to claim 11 wherein the length of the vinyl and maleic monomer-based copolymer block is at least 5 monomeric units before the additional monomer is introduced into the reaction mixture.
- 15 13. Low-molecular weight styrene maleic anhydride (block) copolymer obtainable by a process according to any one of claims 1-12.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/00856

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F222/00 C08F4/00 C08F2/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 135 280 A (COMMONWEALTH SCIENTIFIC AND IND. RESEARCH ORG.) 27 March 1985 ----	
A	US 5 610 249 A (T. OGAWA) 11 March 1997 ----	
A	US 4 551 511 A (A. GOEL) 5 November 1985 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

11 May 1999

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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 99/00856

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